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# Visible light promoted photocatalytic water oxidation: effect of fluctuating light intensity upon reaction efficiency

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Visible light promoted photocatalytic water oxidations were conducted with a synthesized iron oxide nanoparticulate catalyst together with a  $[\text{Ru}(\text{bpy})_3]^{2+}$  light harvesting dye and electron acceptor. With highest intensity set at daylight equivalent levels, the effects of fluctuating illumination upon ongoing reactions were studied and gaseous  $\text{O}_2$  and proton production measured. A light oscillation cycle was identified that significantly increased reaction TOF and quantum yields, which is suggested to arise from improvements in synchronization of the cyclic reaction steps and minimization of light sensitizer self-decomposition.

In tandem with solar photovoltaics, the capture and storage of energy in the form of convenient, inexpensive fuels is an essential goal but remains technically elusive. The design of solar-fuel generation systems with the required efficiency, scalability, and sustainability to be economically viable has clear benefits. Artificial photosynthesis utilizing processes that are akin to Photosystem II (PSII) water oxidation is a vital step towards linking with development of Photosystem I (PSI)-like systems for the complete water splitting reaction and generation of liquid solar fuels.<sup>1-3</sup>

Water oxidation typically utilizes the photocycling light absorbing dye  $[\text{Ru}(\text{bpy})_3]^{2+}$ .<sup>4</sup> The MLCT visible absorption region of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  light sensitizer ranges from ~420-540nm ( $\lambda_{\text{max}}$  454nm) (Fig. 1 inset), hence shorter wavelength visible light is effective in promotion of ruthenium d orbital  $e^-$  onto orbitals associated with a bipyridine ligand to give an excited state  $\text{Ru}(\text{bpy})_3^{2+*}$ .

An electron acceptor ( $\text{Co}(\text{NH}_3)_5\text{Cl}_2$ ) quenches the excited state  $[\text{Ru}(\text{bpy})_3]^{2+*}$ , giving  $[\text{Ru}(\text{bpy})_3]^{3+}$ .<sup>5</sup> An electron donated from a metal oxide catalyst restores the stable  $[\text{Ru}(\text{bpy})_3]^{2+}$  state, and absorbed water is oxidized on the metal oxide surface with the release of  $\text{O}_2$  gas and protons.<sup>6</sup> In total, 4 photons generate 4 protons and an  $\text{O}_2$  molecule.<sup>5,7,8</sup>

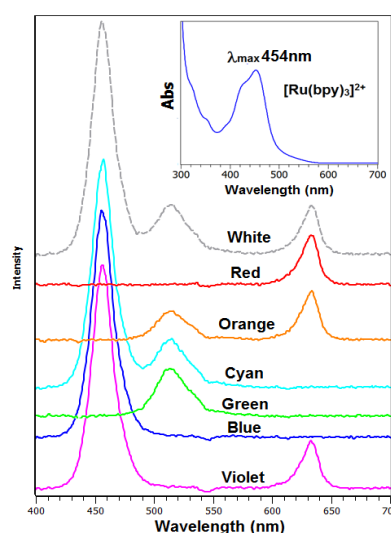


Previously we have investigated the effect of catalyst composition and a range of daylight equivalent light intensities at constant levels over a reaction lifetime.<sup>9</sup> Natural daylight intensity levels vary due cloud cover, diurnal, seasonal and other factors and one aim of this research was determine any effect of fluctuating light intensity upon an ongoing reaction profile and yields.

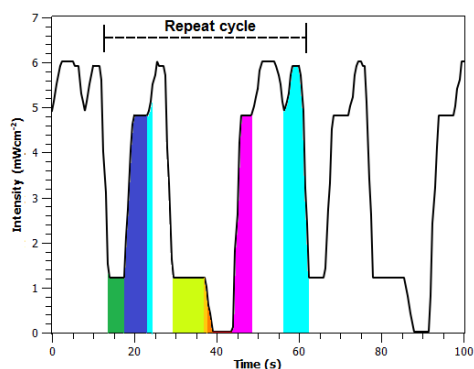
A nanoparticulate iron oxide was prepared as an earth abundant non-toxic catalyst component of the photocatalysis reaction.<sup>10, 11</sup> The oxide was prepared by simple short and moderate temperature calcining methodology utilizing the natural polymer xyloglucan.<sup>12</sup> This acts as a sacrificial agent to

limit particle size during the heating process (catalyst synthesis is described in the ESI<sup>†</sup>). Powder XRD showed the catalyst to be near pure  $\alpha\text{-Fe}_2\text{O}_3$  (JCPDS 013-0534-hematite) together with a trace of  $\gamma\text{-Fe}_2\text{O}_3$  (JCPDS 024-081, maghemite). TEM showed the presence of irregular nanoparticles of ~10-100nm in dimension, EDX showed presence of Fe and O only (Fig. S1a-c, ESI<sup>†</sup>). Braunauer-Emmett-Teller (BET)  $\text{N}_2$  adsorption surface area was measured as  $36.3\text{m}^2/\text{g}$ , with calculated average particle size of ~30nm. Solid state UV-vis spectroscopy of the  $\text{Fe}_2\text{O}_3$  was measured and Tauc plots indicated direct and indirect band gaps of 2.02 and 1.88eV respectively (Fig. S2a-c, ESI<sup>†</sup>). Nanoparticulate hematite has a reported direct band gap of ~2.2eV, the presence of trace levels of  $\gamma\text{-Fe}_2\text{O}_3$  may promote the red-shift in band-gaps observed.<sup>13</sup>

In-situ realtime measurement of  $\text{O}_2$  released into the flask headspace by an accurate optical sensor system and proton generation by pH probe measurement was undertaken.<sup>9, 14</sup> A RGB led capable of cyclic output and also pure colour led's were utilized as light sources. Measurements were made in triplicate with representative yield profiles shown, full experimental and instrumentation details are described in the ESI<sup>†</sup>.



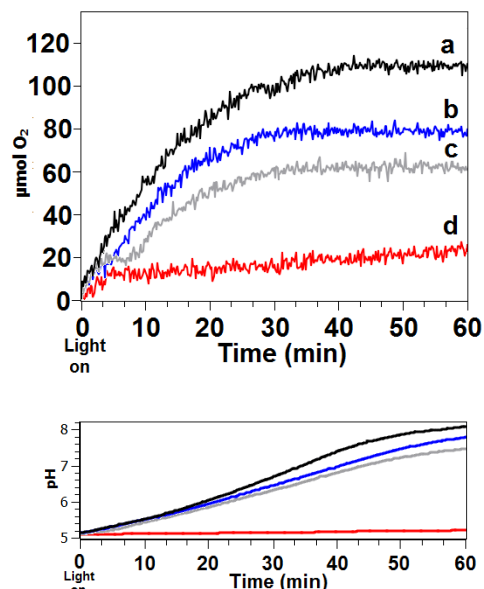
**Fig. 1.** Graph of RGB led light emissions generated in cyclic colour mode. The blue output was used for continuous light reactions. Yellow/orange through to red light lies at the upper edge or outside the absorption region of  $[\text{Ru}(\text{bpy})_3]^{2+}$ . Inset shows absorption spectrum of  $[\text{Ru}(\text{bpy})_3]^{2+}$ .



**Fig.2.** Measured 50s cycling light wavelength/intensity at reaction flask over 420-540nm (matching the  $[\text{Ru}(\text{bpy})_3]^{2+}$  absorption region).  $\bar{x} = 3.3\text{mWcm}^{-2}$  and includes 5s intervals of non-absorbed red light

Photocatalytic water oxidations of 60 min duration were initially conducted using a standard blue led ( $\lambda_{\text{max}}$  455nm) source with measured light intensity at the stirred reaction flask at a daylight equivalent level of  $5\text{mWcm}^{-2}$ .<sup>9</sup> This was then compared to reactions conducted with the led source set to a colour spectrum cycle of 25, 50 or 100s duration repeated for 60min which generated violet through to red including white by mixing of the RGB led sources. Fig. 1 shows the measured RGB wavelengths and relative intensities.

Fig. 2 shows the actual fluctuating light intensity received at the reaction flask of between 0 to  $6\text{mWcm}^{-2}$  (average of  $3.3\text{mWcm}^{-2}$ ) over the  $[\text{Ru}(\text{bpy})_3]^{2+}$  absorption region, using a 50s repeat cycle. Finally, comparison was made to a light source using pure colour  $\lambda_{\text{max}}$  410, 450 and 500nm led sources giving a combined continuous illumination of 400-540nm, to test effects of full saturation of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  absorption region (Fig. S3, ESI<sup>†</sup>).

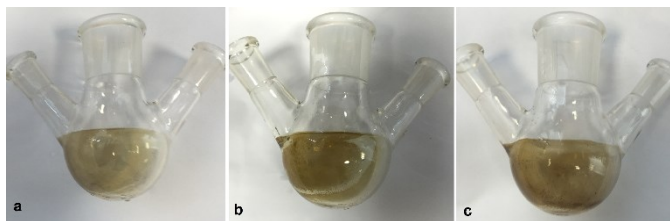


**Fig. 3.** Graph of released  $\text{O}_2$  ( $\mu\text{mol}$ ) against time for photocatalyzed water oxidation reactions with  $\alpha\text{-Fe}_2\text{O}_3$  catalyst (10mg),  $[\text{Ru}(\text{bpy})_3]^{2+}$  (45mg) and  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  (124mg) in 35ml of degassed acetate buffer (pH 5.1, 50mM) using light source of (a) 50s cyclic  $0\text{-}6\text{mWcm}^{-2}$ ; (b)  $5\text{mWcm}^{-2}$   $\lambda 455\text{nm}$ ; (c)  $5\text{mWcm}^{-2}$   $\lambda 400\text{-}540\text{nm}$  and (d)  $\lambda 630\text{nm}$ . Corresponding change in pH with time for these reactions is also shown. (pH increase is caused by decomposition of electron acceptor with liberation of ammonia).

Comparison of measured  $\text{O}_2$  yields and reaction rates showed that 50s cycle gave highest  $\text{O}_2$  yield and reaction rate compared to a 25s and 100s lighting cycle (Fig. S4, ESI<sup>†</sup>). As the repeating 50 second duration fluctuating cycle was in the optimal zone it was used for further comparison to continuous illumination reactions.

Fig. 3 shows gaseous  $\text{O}_2$  generation for 60 min photoreactions using the reagent mixture in stirred  $\text{N}_2$  degassed acetate buffer. Yield profiles for differing lighting conditions including red light as a non-light absorbing control system are shown. Significantly the 50s cyclic fluctuating illumination gave a  $\sim 30\%$  increased  $\text{O}_2$  yield compared to  $5\text{mWcm}^{-2}$  blue light (Fig. 3a,b). This is despite the overall average illumination being  $\sim 30\%$  reduced compared to the continuous blue illumination. Saturation of the absorption region with combined led sources gave further reduced yields compared to both the 50s cyclic and blue sources (Fig. 3c). Red light (together with a low level of ambient light of intensity  $0.1\text{-}0.2\text{mWcm}^{-2}$ ) produced almost no reaction (Fig. 3d). Increase in pH due to capture of electrons from Ru-bpy bonding orbitals in the excited state by the pentamine cobalt acceptor and its subsequent decomposition liberating ammonia corresponds to measured  $\text{O}_2$  generation profiles (Fig. 3).<sup>5</sup>

To establish if lighting effects are replicated using an alternative system, the photocatalyzed water oxidation was repeated using a commercial  $\text{Co}_3\text{O}_4$  nanoparticle powder as catalyst,  $\text{Co}_3\text{O}_4$  is known to be an effective catalyst for water oxidations.<sup>15</sup> Reactions using the 50s cyclic light were compared



**Fig. 4.** Images of rinsed reaction flask following photocatalytic water oxidation using illumination of (a) 50s cyclic; (b) 5mWcm<sup>-2</sup> blue ( $\lambda_{\text{max}}$  455nm) and (c) 5mWcm<sup>-2</sup>  $\lambda$ 400-540nm. A thinner layer of insoluble decomposed [Ru(bpy)<sub>3</sub>]<sup>2+</sup> was obtained with cyclic illumination, whereas saturation of the absorption region resulted in apparent elevated decomposition.

to continuous 5mWcm<sup>-2</sup> blue illumination, an increase in O<sub>2</sub> yield of ~35% combined with increased TOF was obtained with 50s cyclic illumination (Fig. S5, ESI<sup>†</sup>).

The half water splitting reaction is oxidative and thus reagents, in particular organic components are subject to degradation. Cessation of the photocatalytic reaction, which begins after 20-30 min is due to gradual exhaustion of the electron acceptor and also increasing decomposition of the [Ru(bpy)<sub>3</sub>]<sup>2+</sup> dye. In this photoaquation process bipyridine ligands are displaced from the ruthenium and can be observed to form a breakdown product which accumulates as a low solubility dark coloured tar like deposit on the flask surface. Mixture composition is believed to be bipyridine and hydroxylated derivatives of Ru(bpy)<sub>2</sub><sup>2+</sup>.<sup>16-19</sup> An FT-IR comparison of Ru(bpy)<sub>3</sub>Cl<sub>2</sub> and collected degraded bipyridine material was consistent with the suggested breakdown materials (Fig. S6, ESI<sup>†</sup>). The relative degradation processes will be the subject of a separate detailed study.

Significantly, examination of rinsed flasks following 60 min of reaction time suggested that levels of adsorbed hydrocarbon breakdown products was reduced when 50s cyclic illumination was employed compared to continuous illumination (Fig. 4). Catalysis Turn Over Frequencies (TOF's) and Quantum Yields ( $\Phi$ ) were calculated from O<sub>2</sub> generation rate and yields, light intensity and wavelength and are shown on Table 1.

Overall, continuous blue light illumination was satisfactory however saturation of the [Ru(bpy)<sub>3</sub>]<sup>2+</sup> absorption region in intensity and wavelength was detrimental. Significantly, the results suggest an improved balance between a fluctuating illumination pattern and sufficient generation of the [Ru(bpy)<sub>3</sub>]<sup>2+</sup> for the cyclic photoreaction exists using a 50s cycle that includes a ~5s effective zero illumination zone each cycle. Water oxidation at the surface of the heterogeneous moderately active iron oxide catalyst is believed to be the rate limiting step in the photocyclic reaction sequence.<sup>18</sup> Oxygen formation is promoted via electron donation from the metal oxide to the transient [Ru(bpy)<sub>3</sub>]<sup>3+</sup>, hence periods of reduced light influx may allow the rate limiting step to proceed with self-decomposition of excess and unstable oxidized sensitizer minimized.

**Table 1.** Maximum net O<sub>2</sub> generated, calculated TOFs (TOF as mol O<sub>2</sub> per sec per mol (active) metal). Quantum yield  $\phi_{\text{O}_2}$  % = O<sub>2</sub> produced at t = O<sub>2</sub>max @40min/photons absorbed at t = 40 min  $\times$  400% (4 photons absorbed per O<sub>2</sub>).  $S_{\text{BET}}$ , m<sup>2</sup>g<sup>-1</sup>  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> = 36.3, Co<sub>3</sub>O<sub>4</sub> = 35.8. (see Fig.2). (Example calculations are shown in the ESI).

Catalyst (10mg)	Light Source (nm)	O <sub>2</sub> yield (at t=40min) $\mu$ mol	TOF <sub>max</sub> (t = 0-10min) 10 <sup>-4</sup> s <sup>-1</sup>	$\phi_{\text{O}_2}$ % at t=40min
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	cyclic(50s)	108	7.667	45.6
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	cyclic(25s)	69	3.994	29.1
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	cyclic(100s)	55	2.394	23.2
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	455	79	4.792	22.0
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	400-540	62	3.195	17.3
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	630	20	0.7987	5.58
Co <sub>3</sub> O <sub>4</sub>	cyclic(50s)	117	10.44	49.4
Co <sub>3</sub> O <sub>4</sub>	455	75	5.622	20.9

Therefore photocatalysis continued more efficiently for a sustained period, notably the drop away in reaction rate was observed to be offset for ~10min with cyclic illumination (Fig. 3a).

## Conclusions

[Ru(bpy)<sub>3</sub>]<sup>2+</sup> has been extensively employed as the light harvester for photocatalytic water oxidations and is by far the most costly component of the reagent mixture. Thus any improvement of reaction efficiency with reduced sensitizer degradation is of interest. Furthermore, low cost abundant metal oxide catalysts with moderate surface area could be used effectively in these reactions as their activity, in terms of both reaction rate and duration, was enhanced by controlled lighting. We have recently investigated substitution of irreversible electron acceptor with an electron mediator.<sup>20</sup> A long term aim is the combining of these improvements for application and eventual implementation of water oxidation for storable solar fuels.

For this study the main mechanism for the enhanced yields is suggested to be from improved synchronization of the photocyclic reaction steps, which includes reduction in light sensitizer decomposition, balanced with maintaining the ongoing photoreaction with sufficient light influx. For use with natural sunlight, an oscillating prism system can be envisaged to deliver the optimized fluctuating light intensity onto a reaction vessel.

[Ru(bpy)<sub>3</sub>]<sup>2+</sup> is also increasingly being employed as photoredox agent in e.g. organic catalysis,<sup>21-23</sup> photopharmacology,<sup>24</sup> natural product synthesis,<sup>25</sup> and biochemical couplings such as C-S click reactions.<sup>26</sup> Thus effects of light source in terms of both wavelength and continuous versus fluctuating intensity has implications for these wider uses. Our further studies will include a detailed comparative study of light sensitizer decomposition rate and composition

using spectroscopic analysis together with optimization of the cyclic illumination, including use with non-rare earth e.g. Zn-porphyrin light sensitizers.

## Notes and references

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